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Explorations of the magnetization of Ga\textsubscript{1-x}Mn\textsubscript{x}S over a wide range of concentrations, 0.008 < x < 0.18

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Calculations and measurements of the magnetization of Ga\textsubscript{1-x}Mn\textsubscript{x}S, a III-VI diluted magnetic semiconductor crystal, are reported. Results extend over a wide range of concentrations: x = 0.18, 0.13, 0.099, 0.079, 0.062, 0.032, and 0.008. The magnetization was measured at temperatures from 50 to 400 K in magnetic fields up to 7 T. The experimental data are compared with a model of the magnetization that is derived using the energy levels of a singlet Hamiltonian which posits the manganese atoms are not interacting with each other. The Hamiltonian consists of crystal-field, spin-orbit, spin-spin, and Zeeman interactions of the 3d electrons of the Mn\textsuperscript{3+} substitutional ions. The spin-orbit parameter used in the model was \(\lambda = 23\) cm\(^{-1}\), independent of concentration. At smaller values of x the singlet model agreement with the experiment is excellent. For larger values of x and low temperatures the agreement deteriorates somewhat as expected due to the antiferromagnetic coupling of the Mn ions. © 2006 American Institute of Physics.

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I. INTRODUCTION

Diluted magnetic semiconductors (DMSs) have been studied extensively for both II-VI and III-V DMS compounds. Evidence of ferromagnetism has been reported in some instances. The DMS materials are of interest because of their possible utility in laser devices and spintronic applications. A newer class of DMS, the III-VI’s, has received less attention and is the subject of this paper.

Previously a model of the magnetization of III-VI DMSs was formulated\textsuperscript{8} for a single choice of concentration. In this paper the model is compared with the measurements of the magnetization of the III-VI DMS, Ga\textsubscript{1-x}Mn\textsubscript{x}S, over a wide range of concentrations. The crystals were prepared by adding transition-metal ions to the layered III-VI crystalline host, GaS. It is assumed that the transition-metal atoms enter the crystal by random substitution for the group III atoms.

II. SINGLET MODEL HAMILTONIAN

To determine the magnetization we begin by finding the 3d-electron energy levels of the transition-metal ion (Mn\textsuperscript{3+}) embedded in the III-VI crystal host (GaS) and in the presence of an applied magnetic field, B. The choice of Mn\textsuperscript{3+} rather than Mn\textsuperscript{2+} was discussed earlier.\textsuperscript{8} The substitutional manganese atoms are believed to be covalently bonded to their four nearest-neighbor atoms.\textsuperscript{17} The incomplete 3d valence shell of the Mn gives rise to the magnetic moment of the sample. The energy levels of the d electrons of the Mn atom are split by the crystal field among other interactions (see Fig. 1). In this work, only the crystal-field interactions of the 3d electrons with the local neighboring atoms are considered. We have adopted the point-ion approximation which replaces the covalent bonds with ionic bonds where the ions have a formal oxidation state. The 3d-electron energy levels are then determined by the crystal symmetry, distance between ions, bond angles, and the values chosen for the formal oxidation states.

Shown as an inset in Fig. 2 is the orthorhombic crystal structure of the GaS host. The material is layered with van der Waals coupling between layers. One four-atom thick layer is displayed in the inset. The manganese ion resides at the center of an elongated tetrahedron with three Mn–S

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The singlet model assumes that the Mn$^{3+}$ ions are isolated from each other in the GaS lattice. The 3$d$-electron Hamiltonian has the form,

$$H = H_{\text{free-ion}} + H_{\text{crystal}} + H_{\text{spin-orbit}} + H_{\text{spin-spin}} + H_{\text{Zeeman}},$$

where $H_{\text{free-ion}}$ is the Hamiltonian of the free Mn$^{3+}$ ion. Standard expressions are used to represent the spin-orbit, $H_{\text{spin-orbit}}(\lambda)$, the spin-spin, $H_{\text{spin-spin}}(\rho)$, and the Zeeman, $H_{\text{Zeeman}}$ terms in (1). The spin-spin coupling constant that appears in $H_{\text{spin-spin}}$ was set to the free-ion value found in Ref. 18, $\rho=0.18$ cm$^{-1}$. The spin-orbit coupling constant in $H_{\text{spin-orbit}}$ was $\lambda=23.0$ cm$^{-1}$. It should be noted that $\lambda$ was adjusted from the free-ion value to account for the fact that the Mn ion is in a crystal lattice. The operator equivalent crystal-field Hamiltonian takes the form,

$$H_{\text{crystal}} = b[3L_z^2 - L(L+1)] + a(3L_z^4)$$

$$+ [25 - 30(L(L+1)]L_z^2 + 3L_z^2(L+1)^2$$

$$- 6L(L+1)) - d(L_z^z + L_z^2 + L_z^s).$$

Here $L_x = L_x \pm iL_y$ and $L_x$, $L_y$, and $L_z$ are the components of the total electronic orbital angular momentum operator along the Cartesian axes, $x$, $y$, and $z$; $L(S)$ are the total orbital (spin) quantum numbers ($L=S=2$, for the ground-state term and these give a $g$ factor of 1.37 using $J=4$ and the above values of $L$ and $S$). Expressions for the coefficients $a$, $b$, and $d$ are provided in Ref. 8. The last term in (2) is an anticommutator. A $25 \times 25$ matrix representation of the Hamiltonian was obtained using the uncoupled angular momentum basis, $|LSM_L M_S \rangle$, with $L=S=2$ and both $M_L$ and $M_S=0, \pm 1, \pm 2$.

### III. EXPERIMENTAL AND THEORETICAL RESULTS

Previously we reported the magnetization of Ga$_{1-x}$Mn$_x$S for a sample with $x=0.069$. Here we study a broad range of concentrations from boules of bulk crystals grown by the vertical Bridgman method. Magnetization measurements were made from 50 to 400 K in fields up to 7 T using a Quantum Design MPMS XL7 superconducting quantum interference device (SQUID) magnetometer. The diamagnetic susceptibility of the pure GaS crystal was $-3.7 \times 10^{-7}$ emu/g G, and has been subtracted from the experimental data.

Figure 1 illustrates the removal of degeneracy as each part of the Hamiltonian is subsequently turned on. The lowest ten energy levels contribute most to the magnetization. The temperature- and field-dependent magnetization was found using the expression,

$$M(T,B) = \frac{n(x)}{Z} \sum_{i=1}^{N} e^{-\beta E_i} \frac{dE_i}{dB}.$$  

In (3), $\beta=1/k_B T$ (with $k_B$ the Boltzmann constant), $Z$ is the partition function, $N$ is the number of energy levels ($N=25$ for Mn with $3d^5$), $E_i$ is the $3d$-electron energy levels (eigenvalues of $H$), and $n(x)$ gives the number of Mn ions per unit mass of the sample with concentration $x$, i.e., $n(x)$.
FIG. 3. Magnetization of Ga$_{1-x}$Mn$_x$S vs applied field at 300 K (left) and 400 K (right) for concentrations $0.008 < x < 0.18$. The dots are experimental results and the solid curves are the singlet model results.

$$= xN_A/[(1-x)M_{Ga}+xM_{Mn}+M_S].$$ $N_A$ is Avogadro’s number and $M_X$ is the atomic mass of each constituent, $X = \text{Ga, Mn, or S}$.

Results for the magnetization are shown in Figs. 2–4 for concentrations $x = 0.18, 0.13, 0.099, 0.079, 0.062, 0.032,$ and $0.008$. Figures 2 and 3 show the magnetization versus applied field up to 7 T and at constant temperatures of 100, 300, and 400 K. Graphed also are the results of the singlet model in general, the singlet model is seen to give good agreement over the range of concentrations. However, because of Mn–Mn interactions the singlet model is better at lower Mn concentrations than the higher concentrations. Figure 4 graphs the magnetization versus temperature from 50 to 400 K for applied fields of 7 and 1 T (see inset) along with the singlet model results. Again, the agreement is best at low concentrations and the deviation between the theory and experiment is greatest at high concentrations and low temperatures.

IV. CONCLUSION

This paper examines a theoretical model for the magnetization of III-VI DMS over more than an order of magnitude of concentrations and compares the model to the experimental magnetization of Ga$_{1-x}$Mn$_x$S over a wide range of temperatures and fields. The singlet model, which neglects the interaction of Mn ions with each other, was found to agree quite well with the experiment especially in the lower concentration range $(x < 0.10)$. The regions where the singlet model begins to deviate from the experiment corresponds to $x > 0.10$ and lower temperatures. In general, the singlet magnetization is larger than the experimental values. These data suggest, to achieve quantitative agreement in the region where the singlet model overshoots experiment, one should add to the singlet model Hamiltonian a term that reflects antiferromagnetic coupling of manganese spins. The incorporation of Mn doublets$^{19}$ and possibly triplets should help to improve the agreement of model with the experiment, but this goes beyond the singlet treatment of this paper.

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